United States
Environmental Protection
Agency

Technical Fact Sheet – Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Biphenyls (PBBs)

January 2017

TECHNICAL FACT SHEET – PBDEs and PBBs

At a Glance

- Classes of brominated hydrocarbons that serve as flame retardants for electrical equipment, electronic devices, furniture, textiles and other household products.
- Structurally similar and exhibit low to moderate volatility. Lower brominated congeners of PBDE tend to bioaccumulate more than higher brominated congeners.
- May act as endocrine disruptors in humans and other animals. Exposure in rats and mice caused neuro-developmental toxicity and other symptoms.
- The U.S. Department of Health and Human Services states that PBBs are reasonably anticipated to be human carcinogens.
- According to EPA, evidence of carcinogenic potential is suggested for decaBDE.
- EPA has calculated screening levels for PBBs in air, soil and tap water.
- Detection methods include gas chromatography, mass spectrometry and liquid chromatography.
- Potential treatment methods being evaluated at the laboratory scale include debromination using zero-valent iron (ZVI) and nanoscale ZVI, activated carbon treatment and enhanced biodegradation.

Introduction

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a summary of the contaminant groups polybrominated diphenyl ethers (PBDE) and polybrominated biphenyls (PBB), including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information. This fact sheet provides basic information on PBDEs and PBBs to site managers and other field personnel who may encounter these contaminants at cleanup sites.

The manufacture of PBBs was banned in the United States in 1976 after an agricultural contamination incident in 1973 when PBB was accidentally mixed into animal feed, exposing millions of Michigan residents to contaminated dairy products, eggs and meat (ATSDR 2004; NTP 2014). In contrast, PBDEs have been used widely in the United States since the 1970s; however, there is growing concern about their persistence in the environment and their tendency to bioaccumulate (ATSDR 2015; EPA 2009). Since PBDEs and PBBs belong to the same class of brominated hydrocarbons and their chemical structures are similar, they are both discussed in this fact sheet.

What are PBDE and PBB?

- PBDE and PBB are classes of brominated hydrocarbons. They are structurally similar, containing a central biphenyl structure surrounded by up to 10 bromine atoms (ATSDR 2004, 2015).
- PBBs were formerly used as additive flame retardants in synthetic fibers and molded plastics. They are no longer used in the United States (ATSDR 2004; NTP 2014).
- PBDEs are used as flame retardants in a wide variety of products, including plastics, furniture, upholstery, electrical equipment, electronic devices, textiles and other household products (ATSDR 2015; EPA 2009).
- At high temperatures, PBDEs and PBBs release bromine radicals that reduce both the rate of combustion and dispersion of fire (Hooper and McDonald 2000).

What are PBDE and PBB? (continued)

- PBDEs exist as mixtures of distinct chemicals called congeners with unique molecular structures (ATSDR 2015; EPA 2009).
- There are three types of commercial PBDE mixtures, including pentabromodiphenyl ether (pentaBDE), octabromodiphenyl ether (octaBDE) and decabromodiphenyl ether (decaBDE). DecaBDE is the most widely used PBDE globally (ATSDR 2015; EPA 2009).
- The production of octaBDE and pentaBDE in the United States ceased at the end of 2004 after the voluntary phase-out of these chemicals by the only U.S. manufacturer. In 2009, the two U.S. producers and the main U.S. importer of decaBDE announced plans to phase out the compound by the end of 2013 (EPA 2013).
- In 2014, EPA identified 29 potentially functional, viable alternatives to decaBDE for use in select polyolefins, styrenics, engineering thermoplastics, thermosets, elastomers, or waterborne emulsions and coatings (EPA 2014).
- Three types of commercial PBB mixtures were: hexabromobiphenyl (hexaBB), octabromobiphenyl (octaBB) and decabromobiphenyl (decaBB) (ATSDR 2004).
- There are no known natural sources of PBDEs or PBBs; except for a few marine organisms that produce forms of PBDEs that contain higher levels of oxygen (ATSDR 2004; 2015).
- Both PBDE and PBB are structurally similar to polychlorinated biphenyls (PCBs). Both PBDE and PBB are fat-soluble and hydrophobic (Hooper and McDonald 2000; NTP 2014).

Exhibit 1: Physical and Chemical Properties of PBDEs and PBBs
(ATSDR 2004; ATSDR 2015)

Property	PBDEs		
	PentaBDE	OctaBDE	DecaBDE
Chemical Abstracts System (CAS) number	32534-81-9	32536-52-0	1163-19-5
Physical description (physical state at room temperature)	Clear, amber to pale yellow liquid	Off-white powder	Off-white powder
Molecular weight (g/mol)	Mixture	Mixture	959.22
Water solubility at 25°C (µg/L)	13.3 (commercial)	Less than 1 (commercial)	Less than 1
Boiling point (°C)	Over 300	Over 330 (decomposes)	Over 320 (decomposes)
Melting point (°C)	-7 to -3 (commercial)	85 to 89 (commercial)	290 to 306
Vapor pressure at 25°C (mm Hg)	2.2×10^{-7} to 5.5×10^{-7}	9.0×10^{-10} to 1.7×10^{-9}	3.2×10^{-8}
Octanol-water partition coefficient (log K_{ow})	6.64 to 6.97	6.29 (commercial)	6.265
Soil organic carbon-water coefficient (log K_{oc})	4.89 to 5.10 [a]	5.92 to 6.22 [a]	6.80 [a]
Henry's Law Constant at 25°C (atm-m^3/mol)	1.2×10^{-5} [a]	7.5×10^{-8} [a]	1.62×10^{-6} [a]
Property	**PBBs**		
	HexaBB	**OctaBB**	**DecaBB**
CAS number	36355-01-8	27858-07-7	13654-09-6
Physical description (physical state at room temperature)	White solid	White solid	White solid
Molecular weight (g/mol)	627.4	785.2	943.1
Water solubility at 25°C (µg/L)	11	20 to 30	Insoluble
Boiling point (°C)	Not available	Not available	Not available
Melting point (°C)	72	200 to 250	380 to 386
Vapor pressure (mm Hg)	5.2×10^{-8} (at 25°C)	7×10^{-11} (at 28°C)	Not available
Octanol-water partition coefficient (log K_{ow})	6.39	5.53	8.58
Soil organic carbon-water coefficient (log K_{oc})	3.33 to 3.87 [a]	Not available	Not available
Henry's Law Constant at 25°C (atm-m^3/mol)	3.9×10^{-6}	Not available	Not available

Abbreviations: g/mol – gram per mole; µg/L – micrograms per liter; °C – degrees Celsius; mm Hg – millimeters of mercury; atm-m^3/mol – atmosphere-cubic meters per mole.
[a] – Estimated value

What are the environmental impacts of PBDE and PBB?

- PBDEs may enter the environment through emissions from manufacturing processes, volatilization from various products that contain PBDEs, recycling wastes and leachate from waste disposal sites (ATSDR 2015; EU 2001).
- PBDEs and PBBs have been detected in air, sediments, surface water, fish and other marine animals (ATSDR 2004, 2015; EPA 2009).
- Lower brominated congeners of PBDE are more bioavailable, tend to bioconcentrate more, and are more persistent in the environment than higher brominated congeners (ATSDR 2015).
- Higher brominated congeners of PBDE tend to bind to sediment or soil particles more than lower brominated congeners (ATSDR 2015).
- PBDEs and PBBs do not dissolve easily in water and bind strongly to soil or sediment particles. This reduces their mobility in soil, sediment, surface and groundwater, but increases their mobility in the atmosphere, where they are attached to airborne particulate matter (ATSDR 2004, 2015).
- Volatilization from soil surfaces is expected to be low to moderate, depending on the number of bromine atoms. More brominated congeners (higher numbers of bromine atoms) tend to exhibit lower volatilities (EPA 2009; NTP 2014).
- Even though PBDEs and PBBs are relatively stable, they are susceptible to photolytic debromination when they are exposed to ultraviolet light (ATSDR 2004, 2015).
- As of 2016, PBBs had been identified at few sites on the EPA National Priorities List (NPL); however, the number of sites evaluated for PBBs is not well documented (EPA 2016a).
- As of 2016, PBDEs were not identified at any of the current or former hazardous waste sites on the NPL; however, the number of sites evaluated for PBDEs is not well documented (EPA 2016a).

What are the routes of exposure and the health effects of PBDE and PBB?

- Routes of potential human exposure to PBDEs and PBBs are ingestion, inhalation or dermal contact (NTP 2014).
- Since neither PBBs nor PBDEs are produced or used in the United States, the general population can only be exposed from historical releases or products (ATSDR 2004).
- Traces of PBDEs have been detected in samples of human tissue, human blood and breast milk (EPA 2009; He and others 2006)
- The U.S. Department of Health and Human Services (DHHS) states that PBBs are reasonably anticipated to be human carcinogens based on sufficient evidence of carcinogenicity from experimental animal studies (NTP 2014).
- The International Agency for Research on Cancer (IARC) classified PBBs as "probably carcinogenic to humans" (IARC 2016).
- According to EPA, evidence of carcinogenic potential is suggested for decaBDE (EPA 2009; EPA IRIS 2008).
- Neither the DHHS nor the IARC has classified the carcinogenicity of any PBDEs (IARC 2016; NTP 2014).
- Studies on mice and rats show that exposure to PBDEs and PBBs causes neuro-developmental toxicity; weight loss; toxicity to the kidney, thyroid and liver; and dermal disorders (ATSDR 2004, 2015; Birnbaum and Staskal 2004; EPA 2009).
- Studies on animals and humans show that some PBDEs and PBBs can act as endocrine system disruptors and also tend to deposit in human adipose tissue (ATSDR 2004, 2015; Birnbaum and Staskal 2004; He and others 2006; NTP 2014).
- Studies indicate that octaBDE is a teratogen (a prenatal developmental toxin) (Darnerud and others 2001; He and others 2006).

Are there any existing federal and state guidelines and health standards for PBDE and PBB?

- EPA has not derived chronic oral reference doses (RfDs) for PBBs.
- EPA has established the following RfDs for PBDEs (EPA 2016b):

PBDE Congener	Milligrams per kilogram per day (mg/kg/day)
2,2',3,3',4,4',5,5',6,6' decaBDE-209 congener	7×10^{-3}
octaBDE congener	3×10^{-3}
pentaBDE congener	2×10^{-3}
2,2',4,4' - tetrabromodiphenyl ether (tetraBDE-47) congener	1×10^{-4}
2,2',4,4',5,5' - hexabromodiphenyl ether (hexaBDE-153) congener	2×10^{-4}
2,2',4,4',5 - pentaBDE-99 congener	1×10^{-4}

- For decaBDE-209, EPA has assigned an oral slope factor for carcinogenic risk of 7×10^{-4} $(mg/kg/day)^{-1}$ and a drinking water unit risk of 2.0×10^{-8} micrograms per liter (µg/L) (EPA IRIS 2008).
- EPA risk assessments indicate that the drinking water concentration representing a 1×10^{-6} cancer risk level for decaBDE-209 is 50 µg/L (EPA IRIS 2008).
- The EPA has calculated the following screening levels for residential soil, industrial soil and tap water (EPA 2016b):

Chemical	Residential Soil (mg/kg)	Industrial Soil (mg/kg)	Tap Water (µg/L)
PBBs	0.018	0.077	0.0026
decaBDE-209	440	3,300	110
octaBDE	190	2,500	61
pentaBDE	160	2,300	40
tetraBDE-47	6.3	82	2.0
hexaBDE-153	13	160	4.0
pentaBDE-99	6.3	82	2.0

- For PBBs, EPA has also calculated a residential air screening level of 3.3×10^{-4} micrograms per cubic meter (µg/m^3) and an industrial air screening level of 1.4×10^{-3} µg/m^3 (EPA 2016b).
- The Agency for Toxic Substances and Disease Registry (ATSDR) has established a minimal risk level (MRL) of 0.01 mg/kg/day for acute-duration (14 days or less) oral exposure to PBBs and an MRL of 10 mg/kg/day for intermediate-duration (15 to 364 days) oral exposure to decaBDE (ATSDR 2016).
- For lower brominated PBDEs, ATSDR has established an MRL of 0.006 mg/m^3 for intermediate-duration inhalation exposure. In addition, ATSDR established an MRL of 6×10^{-5} mg/kg/day for acute-duration oral exposure and 3×10^{-6} mg/kg/day for intermediate-duration oral exposure (ATSDR 2016).
- Some states, including California, Hawaii, Illinois, Maine, Maryland, Michigan, Minnesota, New York, Oregon, Rhode Island and Washington, have banned pentaBDE and octaBDE. States such as Maine, Maryland, Oregon and Washington have also introduced legislation that bans the sale of certain products containing decaBDE (EPA 2009).
- Various states have adopted screening values or cleanup goals for PBBs in drinking water or groundwater, ranging from 0.0001 to 5 µg/L:

State	Guideline (µg/L)	Source
Indiana	0.026	IDEM 2016
Michigan	0.03	MDEQ 2015
Mississippi	0.00752	MS DEQ 2002
Nebraska	0.0022	NE DEQ 2012
New York	5	NYDEC 2016
Texas	0.0001	TCEQ 2016
West Virginia	0.0022	WV DEP 2009

- Some states have established soil standards or guidelines for PBBs, including Michigan, Mississippi, Nebraska, North Carolina, Texas, West Virginia and Wisconsin.
- The California Environmental Protection Agency (Cal/EPA) has proposed a No Significant Risk Level of 0.02 µg per day for PBBs (Cal/EPA 2013). EPA issued a Significant New Use Rule (SNUR) in 2006 to phase out pentaBDE and octaBDE. According to this rule, no new manufacture or import of these two congeners is allowed after January 1, 2005, without a 90-day notification to EPA for evaluation (EPA 2013).
- On March 20, 2012, EPA proposed to amend the 2006 SNUR by: (1) designating processing of any combination of the six PBDE congeners contained in pentaBDE or octaBDE for any use that is not ongoing, as a significant new use; (2) designating manufacturing, importing or processing of decaBDE for any use that is not ongoing (as of December 31, 2013), as a significant new use; and (3) designating the manufacture, import or processing of any PBDE-containing article as a significant new use (EPA 2013).
- In December 2009, the two U.S. producers and the main U.S. importer of decaBDE committed to end production, import and sales of the chemical for all consumer, transportation and military uses by the end of 2013 (EPA 2012).

What detection and site characterization methods are available for PBDE and PBB?

- Analytical methods used for PBDE detection include gas chromatography (GC)-mass spectrometry (MS) for air, sewage, fish and animal tissues; capillary column GC/electron capture detector (ECD) for water and sediment samples; GC/high resolution MS (HRMS) for fish tissue; and liquid chromatography (LC)-GC-MS/flame ionization detector (FID) for sediments (ATSDR 2015).
- Analytical methods for PBB detection include GC-ECD for commercial samples, soil, plant tissue, water, sediment, fish, dairy and animal feed; high resolution GC (HRGC)/HRMS for fish samples; GC-FID/ECD for soil; and LC-GC-MS/FID for sediment (ATSDR 2004).
- EPA Method 1614 uses isotope dilution and internal standard HRGC/HRMS to detect PBDEs in water, soil, sediment and tissue (EPA 2007).

What technologies are being used to treat PBDE and PBB?

- Research is being conducted at the laboratory scale on potential treatment methods for media contaminated with PBDEs and PBBs.
- Anaerobic bacteria may be utilized to degrade mixtures of decaBDE and octaBDE (He and others 2006; Lee and He 2010).
- Secondary treatment using cationic surfactants may be required to increase the availability of PBDE molecules for reactions with zero valent iron (ZVI) (Keum and Li 2005).
- Laboratory studies are also evaluating the use of bimetallic nanoparticles (BNPs) and nanoscale ZVI (nZVI) for the treatment of PBDEs. Sequential treatment with nZVI and aerobic biodegradation and treatment with iron silver BNPs coupled with microwave energy were both shown to effectively degrade PBDEs (Kim and others 2012, 2014; Luo and others 2012).
- A 2016 laboratory study indicates a tourmaline catalyzed Fenton-like reaction can remove PBDEs from soil (Li and others 2016).
- Bench-scale experiments indicate that electrokinetic remediation may be effective for the treatment of PBDEs in soil (Chun and others 2012).
- The use of activated carbon has also been investigated in a laboratory study for the treatment of PBDE in sediment (Choi and others 2003).

Where can I find more information about PBDE and PBB?

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